

Originator: Kenyon C. Carlson, Manager
ADEQ QA Unit

Contact For
Information: Kenyon C. Carlson, Manager
ADEQ QA Unit

METHOD 515.2

I. SCOPE AND APPLICATION:

This is a gas chromatographic (GC) method applicable to the determination of certain chlorinated acids in ground water and finished drinking water. The following compounds can be determined using this method.

| <u>Analyte</u> | <u>Chemical Abstract Services Registry Numbers (CASRN)</u> |
|---------------------------|---|
| Acifluorfen | 50594-66-6 |
| Benzaton | 25057-89-0 |
| Chloramben | 133-90-4 |
| 2,4-D | 94-75-7 |
| Dalapon | 75-99-0 |
| 2,4-DB | 94-82-6 |
| DCPA acid metabolites (a) | N/A |
| Dicamba | 1918-00-9 |
| 3,5-Dichlorobenzoic acid | 51-36-5 |
| Dichloroprop | 120-36-5 |
| Dinoseb | 88-85-7 |
| 5-Hydroxydicamba | 7600-50-2 |
| 4-Nitrophenol | 100-02-7 |
| Pentachlorophenol (PCP) | 87-86-5 |
| Picloram | 1918-02-1 |
| 2,4,5-T | 93-76-5 |
| 2,4,5-TP (Silvex) | 93-72-1 |

(a) Dacthal monoacid and diacid metabolites included in the method scope;
Dacthal diacid metabolite was used for the validation studies.

II. REAGENTS:

- Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution
- 1:1 hydrochloric acid (HCL) solution

III. MATERIALS:

- 1-liter amber borosilicate sample bottle fitted with screw caps lined with TFE-fluorocarbon.
- Latex gloves and protective eyewear
- Plastic container for disposal of used pipette tips
- Disposable glass pipette and a rubber bulb. Pool and Spa 3-Way Test Strips (Chem Lab Products, Inc.)
- Kim wipes and Paper Towels
- Pliers

IV. PROCEDURE:

1. Remove any attachments such as hoses, screens or aeration devices on the faucet. Inspect the faucet for anything that may fall into the sample container.
2. Open the tap and allow the system to flush for about 10 minutes. This should be sufficiently long enough to allow the water temperature to stabilize and get a representative sample.
3. Adjust the water flow to about 1000 ml/minute or slow enough that no air bubbles purge the sample when collecting from the flowing stream.
4. Remove the cap from the 1-liter container. Do not rinse the container as it has already been acid rinsed and might already contain sodium thiosulfate as a preservative.
5. To fill, tip the bottle to about a 45° angle into the stream of water. Ensure the stream is sufficiently slow so as to be able to anticipate when the bottle is nearly full and thus avoid over flowing. Fill the bottle to within approximately $\frac{1}{2}$ inch of the mouth.
6. Remove the bottle from the flow and recap. Invert the sample bottle five times.

IV. PROCEDURE (continued):

7. Place a chlorine detector strip on a dry opened paper towel. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Moisten the chlorine detector strip with the aliquot from the glass pipette and immediately flick the chlorine detector strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference chlorine range. A determination must be made within 30 seconds.
8. If no chlorine is detected, record results in field notebook and advance to acidification step using 1:1 HCl in item #13.
9. If chlorine is present, add 5 drops of sodium thiosulfate solution, recap the bottle firmly and invert 5 times. Place a chlorine detector strip on a dry opened paper towel.
10. Remove the screw-on cap and obtain an aliquot of the sample using a glass pipette. Thoroughly moisten the chlorine detector strip with the aliquot from the glass pipette and immediately flick the chlorine detector strip once using a sharp wrist motion to shake off the excess water. Compare the strip with the reference chlorine range. A determination must be made within 30 seconds.
11. If no chlorine is detected, record the results in the field notebook and proceed to the acidification step with 1:1 HCl in item #13.
12. Continue the process of adding sodium thiosulfate to the sample, recapping, mixing, and testing until no chlorine is detected. Remember to note the number of drops of sodium thiosulfate added to the water sample in the field notebook.
13. The sample must now be tested for pH concentration. Begin by adding 10 drops of 1:1 HCl (0.5 ml) to the sample and capping. Invert three times and uncap. Dip a strip of pH test paper indicator into the experimental sample and remove, giving the test strip a quick flick of the wrist to shake off excess water. Compare the color change to the reference chart. Determining the pH must be accomplished within a 30 second period. The sample must be acidified to a pH of ≤ 2 . If the sample is adequately preserved, recap the bottle firmly and record the results in the field notebook. Dry the sample bottle, attach the sample/laboratory label to the bottle and secure the chain of custody seal around the cap. Place the sample bottle in the ice chest to cool to 4°C. Duplicate samples not required.
14. If the pH is higher than 2, add 5 drops of 1:1 HCl using a clean glass pipette to the sample, recap, and invert three times.
15. Uncap the vial and retest using a fresh pH test strip.

IV. PROCEDURE (continued):

16. If the pH is ≤ 2 , then record in the field notebook the number of drops need to adequately acidify the sample and place in the ice chest for transportation. If the pH is > 2 , continue the cyclic procedure of adding 5 drops of HCl, capping, inverting three times, uncapping and retesting using a fresh pH strip until the sample is adequately preserved. Determining the pH must be accomplished within a 30 second period. Record the final number of drops required by the sample to acidify to a pH ≤ 2 in the field notebook. Dry the sample bottle, attach the sample label to the bottle and secure the chain of custody seal around the cap. Place the sample bottle in the ice chest to cool to 4°C. Duplicate samples are not required.

V. SAMPLE TRANSPORT:

After obtaining the water samples, attach the completed chain of custody seal around the plastic cap of each 1-liter bottle. The 1-liter bottle must be amber colored to reflect sunlight since some of the pesticides analyzed for in this method are light sensitive and degrade when exposed to ultraviolet radiation. Place the sample bottle into the ice chest for transport. The samples must be chilled and preserved at a temperature of 4°C and maintained at that temperature until analysis. Always use chopped, grated, or dry ice when chilling the voa samples for transportation. Never use “blue ice” as the samples will not adequately chill. Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be at 4°C upon arrival at the laboratory.

VI. SAMPLE PRESERVATION:

The samples must be iced or refrigerated at 4°C and protected from light from the time of collection until extraction. Preservation study results indicate that the sample analytes (measures as total acid), except for 5-hydroxydicamba, are stable in water for 14 days when stored under these conditions. It has been demonstrated that the concentration of 5-hydroxydicamba seriously degrades over a span of 14 days in a biologically active matrix.

VII. DEFINITIONS:

- A. *Sodium Thiosulfate* ($Na_2S_2O_3$): A preservative use to dechlorinate water samples. Reduces free chlorine into acid.
- B. *Eluant*: The solvent that contains the analytes after extraction or desorption.

VIII. SAFETY:

The use of protective eyewear and laboratory quality latex gloves is highly recommended when collecting and preserving samples.

IX. SUMMARY OF METHOD:

METHOD 515.2: liquid/solid extraction: A 250 ml measured volume of sample is adjusted to a pH of 12 using 6 N sodium hydroxide for 1 hour to hydrolyze the derivatives. (Note: Since many of the analytes contained in this method are applied as a variety of esters and salts, it is vital to hydrolyze them to the parent acid prior to their extraction). Extraneous organic material is removed through a solvent wash. The sample is acidified, and the chlorinated acids are extracted with a 47 mm resin based extraction disk. The acids are converted to their methyl esters using diazomethane, or alternatively, trimethylsilyldiazomethane (TMSD). Excess derivatizing reagent is removed, and the esters are determined by capillary column GC equipped with an electron capture detector (ECD).